Molecular Simulations of Electro-Osmosis in Fluid Mixtures Using Semi-Permeable Membranes

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KEYWORDS: electro-osmosis, molecular simulation, separation, diffusion coefficient, electric fields, polar/ionic mixtures.

ABSTRACT

Computer simulations using the method of molecular dynamics have been carried out to study electro-osmosis in polar and ionic solutions. The overall objective was to model and study the separation of a variety of fluid mixtures, by electro-osmosis through semi-permeable membranes at the molecular level. The effects of direction of the external electric field, on the extent of separation have been investigated. The density profiles of the components of the fluid mixtures have been reported to show adsorption near the membrane.

Our results have shown the feasibility of using uniform external electric fields to enhance separation processes such as osmosis and reverse osmosis, in polar solutions. In the past, it was generally believed that these solutions do not undergo electro-osmosis. In the case of ionic solutions, we find a similar increase but only if the direction of the field is reversed periodically. We also show that computer simulation techniques can be a unique tool to improve our understanding of important separation processes such as electro-osmosis, which at present are not well understood.

INTRODUCTION

Separation phenomena such as osmosis, reverse osmosis, ultrafiltration and electroosmosis have significant applications in a wide range of processes in the chemical process industry. Amongst these, electro-osmosis is perhaps the least understood. Electro-osmosis can broadly be defined as the effect of an external field on a system undergoing osmosis or reverse osmosis. Its wide range of applications includes soil purification, water desalination, and drug delivery. There is considerable confusion about its role in non-ionic systems. It is generally implied that uniform electric fields do not lead to electro-osmosis in non-ionic or polar systems [1-5]. This is because uniform fields produce only a torque but no net force, on such systems. A recent note [6] described our preliminary results for model polar systems in which we clearly showed electro-osmosis in these non-ionic solutions. We have now carried out additional studies on model systems consisting of model polar solvents with spherical solutes, and ionic solutes in model spherical or diatomic solvents to observe electro-osmosis effects. We have studied four distinct fluid mixtures, the details of which are summarized in Table 1. The molecular structure of the solute and solvent molecules was chosen to aid in understanding the results. In mixtures of types I and II, we chose the solute to be an uncharged Lennard-Jones (LJ) molecule, so that it is completely unaffected by the uniform electric field. In types III and IV the solvents were chosen to be either LJ or diatomic LJ, again with no charges also to ensure no interaction between the solvent and the external electric field. We have used the molecular dynamics method developed by Murad et al. [7-9] in our work with uniform external electric fields.

METHOD

Computer simulations were carried out to study several fluid mixtures confined by semi-permeable membranes. In our simulations the membrane was formed by tethering a subset of the molecules in their initial FCC configuration to their initial FCC sites by a simple harmonic potential, Φ_T =(1/2)K(δ r)². Here δ r corresponds to the distance between the center of mass of the tethered molecule and the tethering site, and K is the simple harmonic spring

constant. Figure 1 gives a typical simulation setup and location of the membrane for a 216-particle system. All molecules at $x = L_x/2$ and $3L_x/4$ (L_x being the length of the simulation parallelepiped in the x direction) in the initial FCC configuration were designated as the membrane molecules and tethered with a reduced spring constant $K^* = K\sigma^2/\epsilon = 200$. The number of membrane molecules thus depends on the size of the system under consideration and the molecular thickness of the membrane. The site-site interaction potential used is of the form,

$$u_{ij} = 4\varepsilon_{ij}[(r/\sigma)^{-12} - (r/\sigma)^{-6}] + q_i q_i / r$$
 (1)

where ε and σ are Lennard-Jones parameters and r the distance between the sites. coulombic interaction term was included in the potential for charged sites only. In each of the systems studied the molecular weight and Lennard-Jones ε parameters of all molecules were assumed to be identical, since our previous studies have shown the results to be much more sensitive to the molecular size [7]. For cross interactions, the Lorentz-Berthelot mixing rules were used. In a few cases $\eta_{solute-wall}$ (cross term for σ_{ij}) was varied to ensure the impermeability of the membrane to solute molecules. The interaction potential was truncated at 3 σ . We also used the reaction field method to include the effect of long range interactions and found that the dynamic behavior was unaffected by such long range forces. This has also been seen by others using ionic systems [10]. All simulations were carried out with and without (spatially) uniform external electric fields. The strength of the electric fields was also varied, depending on the system studied. We are aware that the electric fields used by us are somewhat higher than those used in experiments. This was done to see the effect of these fields clearly in the usual simulation time frame of about 10^{-10} seconds. In a normal experimental time scale, we believe these effects would be seen in field strengths which are experimentally accessible.

Preliminary studies of the effect of electric field in a polar system containing model homonuclear diatomic solvent molecules and spherical LJ solute and membrane molecules were reported recently [6]. In our preliminary study [6] the size parameters for the solvent sites and membrane molecules were fixed at 0.7σ and 1.0σ respectively, with a $\eta_{solute-wall}$ =

1.25 (σ , ϵ , and m from here on refer to the LJ parameters and molecular weights of the solute molecules). The bond length of the diatomic was fixed at $1 = 0.384\sigma$ and the charges on each of the sites at $\pm 8(\epsilon\sigma)^{1/2}$. Both sites of the diatomic were otherwise identical. The model heteronuclear mixtures studied consisted of (polar) solvent molecules and LJ solutes, similar to the homonuclear mixtures, except the solvent was heteronuclear. The molecular size of the first site was fixed at 0.8 σ which was negatively charged, while the smaller site's size was 0.6 σ and was positively charged (The average σ of the two sites was identical to the σ of the model homonuclear solvent sites). In addition, the larger site contained 57 percent and the smaller site 43 percent of the total mass of the molecule. Simulations for the systems I and II were carried out for 216 particles with a FCC setup density of $0.5/\sigma^3$ and temperature $T=4.5(\epsilon/k)$. The actual densities of the solvent compartment may be different, depending upon the actual number of solvent molecules (see results section). The system dimensions were $L_x = 2L_y = 2L_z$ = 12σ , where L_y and L_z represent the length of the simulation box in the y and z directions respectively. Each simulation consisted of 330,000 time steps (inclusive of 30,000 initiation steps) of size $\delta t = 0.0005 (m\sigma^2/\epsilon)^{1/2}$. Simulations were performed for three cases: zero external field, a uniform electric field $E_d = (E_x^2 + E_y^2 + E_z^2)^{1/2}$, and a uniform field of the same strength but only in the x direction. The field strengths were varied between 1 and 4 in the units of $(\epsilon/\sigma^3)^{1/2}$. The temperature, solute concentration and system density were all varied in our studies.

Mixtures of types III and IV consisted of spherical charged LJ solutes (ionic) and spherical LJ membrane molecules. Type III contained diatomic solvent molecules (with 2 identical active LJ sites) while the solvent in type IV was comprised of spherical LJ solvent molecules. Simulations were carried out for 432-particle systems for type III mixtures and 864-particle systems for Type IV mixtures. The system dimensions in case III were $L_x = 4L_y = 4L_z = 24\sigma$ while in case IV they were $L_x = 8L_y = 8L_z = 48\sigma$. The initial FCC setup density was varied between $0.4/\sigma^3$ and $0.6/\sigma^3$. The membrane pore sizes were fixed to allow solvent molecules to permeate, while preventing the solute molecules from permeating. The

simulations for the mixtures of type III, which contained homonuclear diatomic solvent particles ($\sigma_{solvent} = 0.5\sigma$ and bond length $l = 0.148\sigma$) were performed at $T = 4.5(\epsilon/k)$ and consisted of 20,000 initiation steps followed by one million time steps, both of $\delta t =$ $.0005 (m\sigma^2/\epsilon)^{1/2}$. Simulations for the type IV mixtures which contained LJ solvent particles $(\sigma_{solvent}=0.45\sigma)$ were carried out with a larger time step of $\delta t=0.001(m\sigma^2/\epsilon)^{1/2}$. The magnitude of the charges on the solutes was varied to study their effect on the system's response to electric fields. Each system had equal number of positively and negatively charged solute ions, with all other parameters of the ions being identical. Simulations for these two ionic systems were carried out for a longer duration (see above), as the response to the electric field was rather indirect. We believe the solvent molecules are dragged along as the ions respond to the electric field. In addition to applying a direct uniform electric field (in the x direction), the direction of the field was reversed periodically during the length of the simulation. This was done to prevent the solute ions from clogging the pores in the membrane. The time for reversing the field roughly corresponded to the time taken by these solute particles to move less than one-half length of the cube. The effect of temperature was also studied by performing runs at several temperatures. The movement of the solvent molecules across the membrane, their mean squared displacements, orientation with respect to the membrane and density profiles across the length of the cubes were all recorded. All results will be reported in reduced units based on solute LJ (ε and σ) parameters.

RESULTS AND DISCUSSIONS

The primary objective of this study was to examine the role of spatially uniform external electric fields on systems undergoing reverse osmosis. For all the four types of systems under consideration, 36 molecules constituted the two membranes. The solution compartment consisted of N_B solute molecules and remaining solvent molecules. The density in the solvent compartment was varied. This led to an initial pressure difference between the solute and solvent compartment. Depending on the magnitude of this pressure difference, osmosis or reverse osmosis resulted [8]. Most results shown here correspond to an overall

system density of $0.5/\sigma^3$. A few simulations were performed at other densities as shown in Table 1. During the simulation the number of solvent molecules permeating the semi-permeable membrane were monitored. $N_C(t)$ denotes the number of solvent molecules which moved from the solution to the solvent compartment at time t. The membrane was designed not to allow any solute molecules to permeate it, although occasionally one or two did permeate, as is the case in real experiments.

Simulations for systems of types I and II, consisting of 216 particles had either 10 or 30 solute molecules (hence 80 or 60 solvent molecules) in their solution compartment. The results obtained were similar at both concentrations; although equilibrium was reached sooner in the higher concentration systems. From the initial FCC setup of 90 molecules in the solvent compartment, either all the molecules were removed (creating a vacuum) or only 45 molecules were removed. This provided two distinct initial pressure differences between the compartments but still ensured reverse osmosis in the system. Results for systems of type I have been reported in [6], so we will not repeat them here. Figure 2 shows the <N_C(t)> as a function of time for a type II system, where <N_C(t)> corresponds to N_C(t) averaged over a short time Δ ,

$$\langle N_C(t) \rangle = \frac{1}{\Delta} \int_{t-\Delta/2}^{t+\Delta/2} N_C(t') dt'$$
 (2)

Here $\Delta=10 (m\sigma^2/\epsilon)^{1/2}$, $N_B=10$, initial number of molecules in solvent compartment = 0, and the temperature of the system was $4.5\epsilon/k$. The averaged crossings into the solvent compartment are shown for three cases: zero electric field, a uniform electric field E_x of strength $3.0(\epsilon/\sigma^3)^{1/2}$ perpendicular to the membrane, and a uniform electric field $E_d=3.0(\epsilon/\sigma^3)^{1/2}$ in the diagonal direction. The Figure shows an increase in the rate of reverse osmosis in the presence of the uniform electric fields. The x component of the mean squared displacement of the solvent molecules, which is related to the diffusion coefficient D_x (in a direction perpendicular to the membrane), is shown as a function of time in Figure 3 for the same system. This also implies greater membrane permeability [7] in the presence of an electric field. Although our simulations are not long enough to confirm this, at $t \to \infty$, it is conceivable and likely that $< N_C >$ would be equal for all three cases [6].

The increase in rate of reverse osmosis we believe is due to fewer clusters of the polar solvents. The external fields tend to make larger molecular clusters less energetically favorable and, hence, aid in permeation. The increase in permeation cannot be attributed to the orientations of the diatomic solvent molecules due to the electric fields. The preferred orientation of the molecules for permeation is perpendicular to the plane of the membrane. The fractional distribution of solvent molecules oriented in this direction (defined by us as those with the x component of the unit vector along the molecular axis, $|e_x| \ge 0.9$) oscillates around the random value of 0.1 for systems that are not subjected to electric fields. For the case shown in Figure 2, with a field in the x direction, we observe a higher fraction of 0.15. With the application of the field in the diagonal direction, this value is even lower than 0.1, which would make it on an average more difficult for the solvent molecules to permeate the membrane. The results seen in Figure 2 show clearly an increase in permeation in both cases, which leads to our conclusion that the increase in rate of reverse osmosis is not directly a molecular orientation effect but rather a molecular declustering effect. Simulations performed at lower temperatures showed the same trend; an increase of rate of reverse osmosis in the presence of a uniform external field.

In systems of types III and IV, the effect of the uniform electric field on the increase in permeation of the membrane by the solvent molecules observed must be an indirect effect, since here the solutes were charged ions and the solvents uncharged. In type III systems there were 54 solute molecules (27 each of anions and cations), thus maintaining the overall neutrality of the system. This resulted in 144 (198-54) solvent molecules in the solution compartment. Type IV systems contained 44 solute molecules and 370 (414-44) solvent molecules in the solution compartment. In both cases there were no molecules initially on the solvent side. These simulations were generally longer than those of type I and II since, as mentioned earlier, electro-osmosis is an indirect effect.

Figure 4 shows <N_C(t)> evaluated for $\Delta = 25 (m\sigma^2/\epsilon)^{1/2}$ plotted against time for a type III mixture with $q_{solute} = \pm 3 (\epsilon \sigma)^{1/2}$, and $T = 4.5\epsilon/k$. Here a field strength of $E_x = 2.0 (\epsilon/\sigma^3)^{1/2}$ was applied which in some simulations was also reversed every $2.5 (m\sigma^2/\epsilon)^{1/2}$ seconds. There is clear evidence of electro-osmosis, but only in the case when the direction of the electric field

was reversed periodically. This is necessary we believe, to prevent the pores in the membrane from being clogged by the solute ions, as the solute ions are larger than the pores in the membrane. Thus when a uniform electric field in a single direction was applied, these solute ions interacted with the field, traveled across the solution compartment and clogged the pores in the membrane. This inhibited further permeation of the membrane by the solvent molecules. This is shown in Figure 5 and 6 which show the density profiles of solute molecules and solvent molecules respectively at time $t = 920 (m\sigma^2/\epsilon)^{1/2}$, for the type IV system (q_{solute} = $\pm 2(\epsilon\sigma)^{1/2}$, $T=3.5\epsilon/k$). The Figures show results for no electric field, a fixed electric field, E_x = $1.0(\epsilon/\sigma^3)^{1/2}$ and an electric field of the same strength but with the direction periodically reversed every $22.5(m\sigma^2/\epsilon)^{1/2}$ seconds. The solute ions are more evenly distributed in the solution compartment when the external field is reversed periodically and this as expected leads to a higher level of electro-osmosis. Similar results were observed for type III mixtures. The increase in the rate of solvents permeating the membrane is we believe due to solvent molecules getting dragged along with the charged solute molecules, as the solutes move as a result of their interaction with the external electric field [11]. Systems containing solutes with weaker charges required higher field strengths and more frequent reversing of the electric field to observe comparable levels of electro-osmosis. Studies were carried out at other temperatures, and the results showed similar trends as those discussed here.

CONCLUSIONS

We have reported a comprehensive study on the effect of uniform electric fields on several systems undergoing reverse osmosis. We have demonstrated using the method of molecular dynamics, the feasibility of using such fields to enhance separation processes using reverse osmosis. This is observed for both polar and ionic solutions. Our results thus point out a useful technique for increasing the rate of separation using reverse osmosis. This is especially true for polar solutions, where electro-osmosis has not been widely used in the chemical industry.

NOMENCLATURE

- K Simple harmonic spring constant
- L_{α} Length of the simulation system in the a direction ($\alpha = x,y,z$)
- u Interaction potential
- q_{α} Charge on site α
- r Intermolecular distance between two sites
- T Temperature of the system
- 1 Bond length of diatomic solvent
- E Applied electric field
- m Mass of the solute
- k Boltzman's constant
- N_B Number of solute molecules in the solution compartment
- N_C Net number of solvent molecules that move from the solution compartment to the solvent compartment during simulation
- D_X Diffusion coefficient perpendicular to the semi permeable wall
- ϕ_T Simple harmonic potential
- σ LJ size parameter of the solute
- ε LJ energy parameter of the solute
- η Lorentz-Berthelot binary interaction size parameter
- δt Length of simulation time step

ACKNOWLEDGEMENTS

This research was supported by grants from the Division of Chemical sciences, US Department of Energy (DE-FG02-96ER14680). We thank K. Oder for helpful discussions.

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TABLE I: General characteristics of the fluid mixtures studied

	I	II	III	IV
Solute	Spherical LJ	Spherical LJ	Charged Spherical LJ	Charged Spherical LJ
Solvent	Homonuclear polar	Heteronuclear polar	Homonuclear neutral	Spherical LJ
	diatomic	diatomic	diatomic	
Membrane	Spherical LJ	Spherical LJ	Spherical LJ	Spherical LJ
Number of particles	216	216	432	864
System dimensions	$L_x = 2L_y = 2L_z = 12\sigma$	$L_x = 2L_y = 2L_z = 12\sigma$	$L_x = 4L_y = 4L_z = 24\sigma$	$L_x = 2L_y = 2L_z = 48\sigma$
Number of solute particles	10, 30	10, 30	54 [*]	44*
Site charge $(\varepsilon\sigma)^{1/2}$	$q_{\text{solvent}} = \pm 8, \pm 4$	$q_{solvent} = \pm 8, \pm 4$	$q_{\text{solute}} = \pm 2, \pm 3, \pm 4$	$q_{\text{solute}} = \pm 1, \pm 2, \pm 3$
Field strength $(\varepsilon/\sigma^3)^{1/2}$	2, 4	2, 3	1, 2, 3	1, 2
System temperature (ε/k)	4.5, 3.0	4.5, 3.0	5.5, 4.5, 3.5	3.5, 2.5
System density $(1/\sigma^3)$	0.5, 0.4	0.5, 0.4, 0.6	0.5, 0.4	0.5, 0.4
η _{solute-wall}	1.25	1.25	1.0	1.0

^{*} Includes equal number of identical positive and negative solute ions.

FIGURE CAPTIONS

- Figure 1. The (a) xy and (b) three dimensional view of a simulation system showing the structure of the membrane and solvent/solution compartments.
- Figure 2. Average number of solvent molecules $\langle N_C \rangle$ permeating the membrane in a type II mixtures as a function of time.
- Figure 3.The mean squared displacement of the solvent molecules in a direction perpendicular to the membrane plane, as a function of time in a system of type II. Legend as in Figure 2.
- Figure 4. Average number of solvent molecules <N_C> permeating the membrane in a type III system shown as a function of time. R refers to the cases when the direction of the field is periodically reversed.
- Figure 5. Density profile of solute anions and cations in a type IV mixture at $t = 920 (m\sigma^2/\epsilon)^{1/2}$, across the length of the parallelepiped.
- Figure 6. Density profile of solvent molecules at $t = 920 (m\sigma^2/\epsilon)^{1/2}$, across the length of the parallelepiped in a type IV mixture.

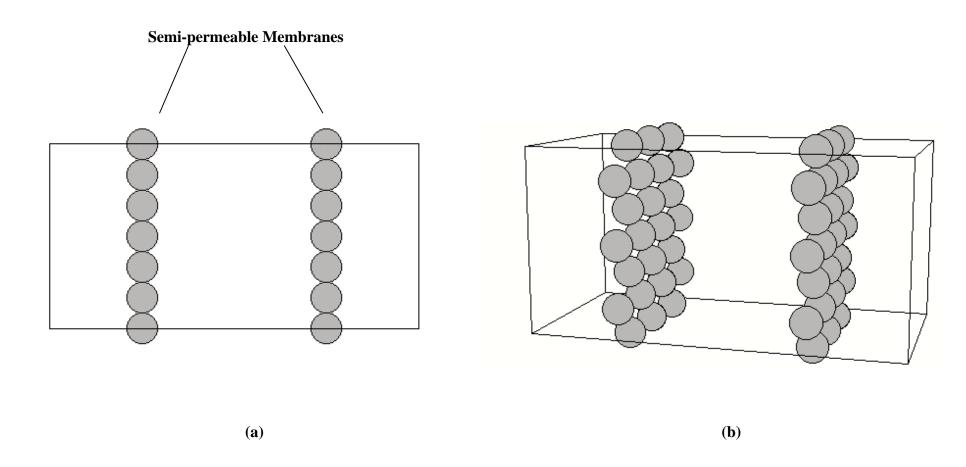


FIGURE 1.

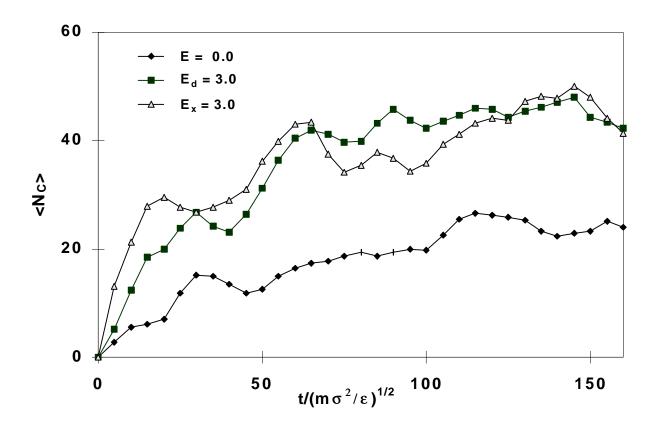


FIGURE 2.

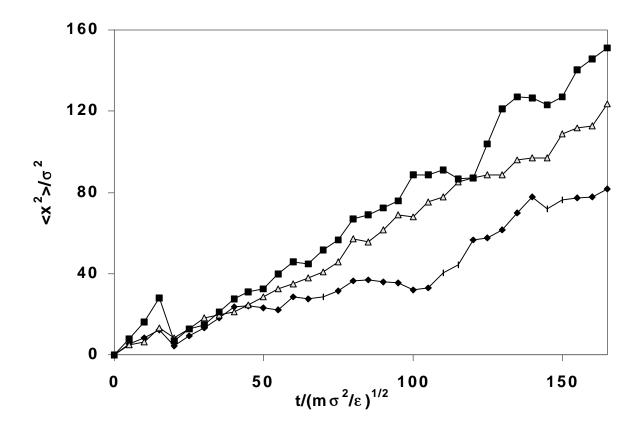
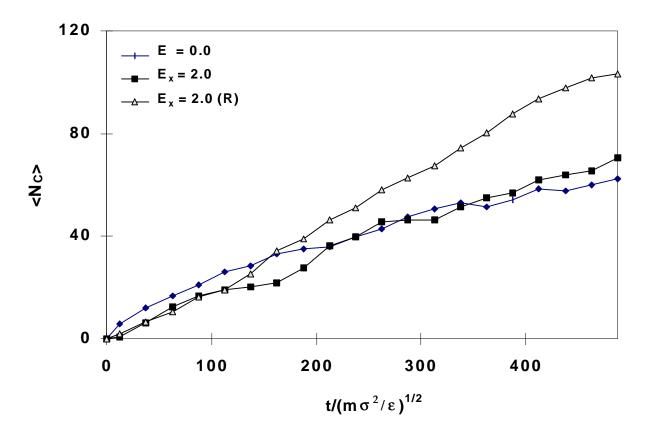


FIGURE 3.



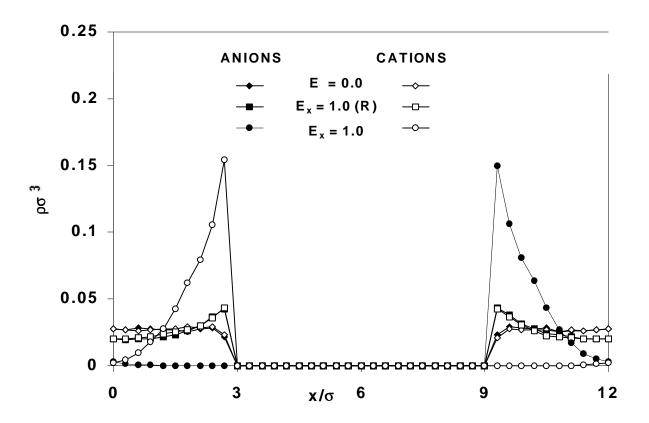


FIGURE 5.

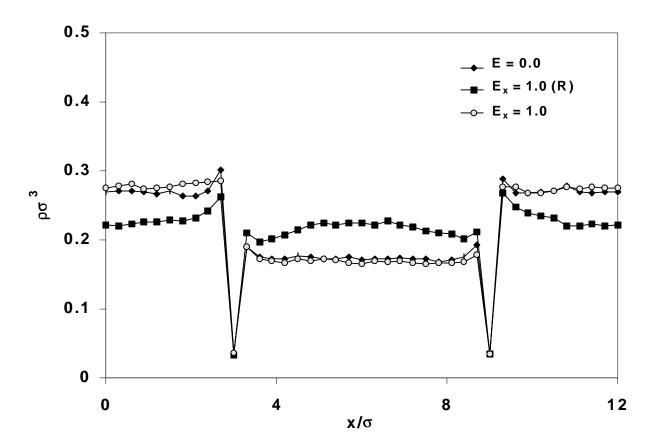


FIGURE 6.